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Hartree-Fock study of the Anderson model coupled to a boson field; mixed valence states

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We generalize the Anderson model of magnetic impurities in metals, introducing a local coupling between the impurity orbital and a boson field. A systematic finite-temperature Hartree-Fock and random-phase-approximation investigation is presented; particular attention is paid to the problem of multiple solutions of the Hartree-Fock equation, and the various phase transitions in parameter space appearing in this approximation. Regions of slow interconfigurational valence fluctuations are identified, and applications to the problems of mixed-valence rare-earth materials and resonant two-electron states in amorphous materials are suggested.

I. INTRODUCTION

This work presents a systematic investigation in the mean-field approximation of the properties of an extension of the Anderson model[1] of a magnetic impurity in a metal, in which a boson field has been coupled to the impurity.

We initially derived this model using Tomonaga boson[2] methods from a combination of the Anderson model and a single-site isolated rare-earth impurity version of the Falicov-Kimball model,[3] in an attempt to investigate model systems showing the "mixed-valence" phenomenon.[4] This derivation is presented elsewhere,[5] but sketched briefly in Sec. VIII. Applications of the model are not however restricted to this: another suggested interpretation is as a model for resonant two-electron centers, which have been postulated to play an important role in amorphous materials with strong electron-phonon coupling.[6]

In the mean-field approximation, various different phases and phase transitions appear in the parameter space of the model. These are of course artifacts of the approximation; the properties of finite systems coupled to a Fermi sea with its infinite number of low-energy excitation modes must change smoothly as the parameters are varied. Nevertheless, the phase diagrams are very suggestive, and, when suitably reinterpreted, indicate what we can expect an exact treatment to yield.

The bulk of this paper is devoted to an investigation of the interesting properties of this model in its own right, without reference to particular interpretations. Applications are suggested at the end of the paper. Section II reviews the model; Sec. III derives a variational functional for the free energy, and the Hartree-Fock (HF) equations; Sec. IV explores the stability of the various types of solutions, and determines the HF phase diagram; Sec. V supplements this by examining the stability of the spectrum of collective excitation modes in the random-phase approximation; Sec. VI discusses the relation of mean-field results to the true properties, with emphasis on the interesting regimes of slow interconfigurational valence fluctuations and the Kondo effect; Sec. VII shows how composite systems, treated as an assembly of isolated impurities, may be pinned precisely in a valence fluctuation state; finally, Sec. VIII summarizes the results, and briefly discusses the possible physical realizations of the model, namely mixed-valence compounds and two-electron centers.

II. MODEL

The Anderson model[1] has found many applications in the study of magnetic impurities in metals and the Kondo effect. In the usual second-quantized notation, its simplest, nondegenerate form is

$$H = H^0 + E_d \sum_\sigma n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + V \sum_\sigma (\psi_\sigma^\dagger c_{d\sigma} + \text{H.c.}), \tag{1}$$

$$H^0 = \sum_{k\sigma} \epsilon_k n_{k\sigma}, \quad \psi_\sigma = \sum_k v_k c_{k\sigma}.$$

The fermion operators $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) create (destroy) particles in orbitals $|k\sigma\rangle$ of a noninteracting Fermi gas; $c_{d\sigma}^\dagger$ creates a particle in a localized "extra orbital" orthogonal to the $|k\sigma\rangle$. As this extra orbital is visualized as being very localized, while the $|k\rangle$ are extended, correlation effects between electrons in the local orbital will play a more important role than those in the Fermi gas; interaction terms in the Fermi gas are neglected, but an interaction term $U n_{d\uparrow} n_{d\downarrow}$ between localized electrons is retained. A hopping matrix element V connects the extra orbital and $\psi^\dagger$, a local combination of Fermi sea orbitals having the same point symmetry as $c_d^\dagger$. The Fermi-sea orbitals may be analyzed into point-symmetry-group representations around the site of the extra orbital;

only those with the same symmetry as the impurity are relevant to the problem, and the others have been discarded; hence H^0 is essentially nondegenerate, as is the impurity.

We have generalized this model by adding a *boson field*, and a linear term coupling it to the charge in the extra orbital.

$$H^{\text{boson}} = \sum_q \omega_q a_q^\dagger a_q , \tag{2}$$

$$H^{\text{boson-fermion}} = g \sum_\sigma n_{d\sigma} \sum_q (\alpha_q a_q + \text{H.c.}) \tag{3}$$

Two possible interpretations of the bosons are discussed in Sec. VIII: for the time being we merely note that the boson spectrum should be thought of as extending down to zero energy.

As interactions in the model are essentially local, H^0 and H^{boson} may both be completely characterized by their spectral densities projected on to the relevant local combination of states. For H^0 this is

$$\nu(\omega) = \pi \sum_k |v_k|^2 \delta(\omega - \epsilon_k) . \tag{4}$$

For H^{boson}

$$f(\omega) = \pi \sum_q |\alpha_q|^2 \delta(\omega - \omega_q) . \tag{5}$$

Because of their normalization, both $\nu(\omega)$ and $f(\omega)$ must have some high-energy cutoff or bandwidth: if V is small only the boson bandwidth will turn out to have any direct relevance to the properties of the model.

We will use a mean-field approach, decoupling fermions and bosons. This will be valid if the relaxation time for the boson field, given by the boson bandwidth, is either much shorter or longer than the time for electrons to "hop" on or off the extra orbital, given by the resonance width $\Delta \sim V^2 \nu(\epsilon_F)$.

III. MEAN-FIELD THEORY: A VARIATIONAL APPROACH TO THE FREE ENERGY

A finite-temperature version of Hartree-Fock theory may be based on the free-energy inequality[7]

$$F(H^{\text{eff}}) + \langle H^{\text{corr}} \rangle_{H^{\text{eff}}} \geq F(H^{\text{eff}} + H^{\text{corr}}) . \tag{6}$$

This is the generalization of the Rayleigh-Ritz inequality, and holds for any partition of the Hamiltonian into $H^{\text{eff}} + H^{\text{corr}}$. We take H^{eff} to be a single-particle effective Hamiltonian; H^{corr} is the residual interaction term. The Hartree-Fock equations are obtained by varying H^{eff}, and finding stationary values of the left-hand side of (6).

In our case, it is sufficient to introduce six variational degrees of freedom; the parameters $\langle a_q \rangle, \langle a_q^\dagger \rangle, \langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$. The four quantities $\langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$ may be regrouped into a mean charge, $\langle N_d \rangle = \frac{1}{2} \delta_{\sigma\sigma'} \times \langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$ (summation over σ, σ' implied), and a mean spin vector $\langle \vec{S}_d \rangle = \frac{1}{2} \vec{\sigma}_{\sigma\sigma'} \langle c_{d\sigma}^\dagger c_{d\sigma'} \rangle$, where $\vec{\sigma}$ are the Pauli matrices. By a suitable rotation of the spin coordinates, $\langle \vec{S}_d \rangle$ may be lined up along the z axis, making $\langle c_{d\sigma}^\dagger c_{d-\sigma} \rangle$ vanish.

We write

$$b_q = a_q - \langle a_q \rangle , \tag{7}$$

$$E_\sigma^{\text{eff}} = E_d + U \langle n_{d-\sigma} \rangle + g \sum_q (\alpha_q \langle a_q \rangle + \text{H.c.}) \tag{8}$$

The Hamiltonian, $H^{\text{eff}} + H^{\text{corr}}$, can be written in the form

$$H^{\text{eff}} = -\sum_q \omega_q \langle a_q^\dagger \rangle \langle a_q \rangle + U \langle n_{d\uparrow} \rangle \langle n_{d\downarrow} \rangle + g \sum_\sigma \langle n_{d\sigma} \rangle \sum_q (\alpha_q \langle a_q \rangle + \text{H.c.}) + \sum_q \omega_q b_q^\dagger b_q$$
$$+ \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_\sigma E_\sigma^{\text{eff}} n_{d\sigma} + V \sum_\sigma (\psi_\sigma^\dagger c_{d\sigma} + \text{H.c.}) + \left[\sum_q \left(\omega_q \langle a_q \rangle + g \alpha_q^* \sum_\sigma \langle n_{d\sigma} \rangle \right) b_q^\dagger + \text{H.c.} \right], \tag{9}$$

$$H^{\text{corr}} = U(n_{d\uparrow} - \langle n_{d\uparrow} \rangle)(n_{d\downarrow} - \langle n_{d\downarrow} \rangle) + g \sum_\sigma (n_{d\sigma} - \langle n_{d\sigma} \rangle) \sum_q (\alpha_q b_q + \text{H.c.}) \tag{10}$$

It is easily shown that the variational equation for $\langle a_q \rangle$ is only satisfied when the linear boson term in (9) (square brackets) vanishes, so we set

$$\langle a_q \rangle = -\frac{g \alpha_q^*}{\omega_q} \sum_\sigma \langle n_{d\sigma} \rangle . \tag{11}$$

The displacement of the boson field gives rise to an effective attractive interaction between electrons, with coupling constant C,

$$C = 2g^2 \sum_q \frac{|\alpha_q|^2}{\omega_q} \quad (>0) , \tag{12}$$

and the effective Hamiltonian reduces to

$$H^{\text{eff}} = \tfrac{1}{2} C\Big(\sum_\sigma \langle n_{d\sigma}\rangle\Big)^2 - U\langle n_{d\uparrow}\rangle\langle n_{d\downarrow}\rangle + \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_\sigma E_\sigma^{\text{eff}} n_{d\sigma} + V\sum_\sigma (\psi_\sigma^\dagger c_{d\sigma} + \text{H.c.}) + \sum_q \omega_q b_q^\dagger b_q , \tag{13}$$

$$E_\sigma^{\text{eff}} = E_d - C\langle n_{d\sigma}\rangle + (U-C)\langle n_{d-\sigma}\rangle . \tag{14}$$

This effective Hamiltonian H^{eff} ($\langle n_{d\sigma}\rangle$) is quadratic in fermions; in the Appendix its free energy $F(H^{\text{eff}})$ is evaluated in closed form, using Green's-function equation-of-motion techniques and coupling-constant integration. We find, for arbitrary E',

$$F(H^{\text{eff}}) = F_0(E') - U\langle n_{d\uparrow}\rangle\langle n_{d\downarrow}\rangle + \tfrac{1}{2} C\Big(\sum_\sigma \langle n_{d\sigma}\rangle\Big)^2 - \frac{1}{2\pi i}\oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1}\sum_\sigma \ln\Big(\frac{\omega - E_\sigma^{\text{eff}} - \Sigma(\omega)}{\omega - E'}\Big) . \tag{15}$$

$E_\sigma^{\text{eff}}(\langle n_{d\sigma}\rangle)$ is given by (14) and

$$\Sigma(\omega) = \frac{V^2}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\nu(\omega')}{\omega - \omega'} , \tag{16}$$

$$F_0(E') = F\Big(\sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_\sigma E' n_{d\sigma} + \sum_q \omega_q b_q^\dagger b_q\Big) . \tag{17}$$

The contour Γ circles the real axis from $(-\infty - i\epsilon) \to (+\infty - i\epsilon) \to (+\infty + i\epsilon) \to (-\infty + i\epsilon) \to (-\infty - i\epsilon)$. It will be convenient to define the function

$$n(x) = \frac{1}{2\pi i}\oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1}\frac{1}{\omega - x - \Sigma(\omega)} . \tag{18}$$

The expectation value of $n_{d\sigma}$ in the system H^{eff} is then given by

$$\langle n_{d\sigma}\rangle_{H^{\text{eff}}} \equiv \text{Tr}(n_{d\sigma} e^{-\beta H^{\text{eff}}})/\text{Tr}(e^{-\beta H^{\text{eff}}}) = n(E_\sigma^{\text{eff}}) . \tag{19}$$

$n(x)$ can be shown to be monotonic decreasing from 1 to 0 (Fig. 1): furthermore, we will characterize it by assuming $n'(x)$ has a unique minimum value of $-1/U_c$ at $x = x_c$, near the Fermi level. This behavior is very general and insensitive to the details of the spectral density $\nu(\omega)$, provided it is not too pathological. For the canonical case[1] of a quasiflat spectral density $\nu(\omega) \sim \text{const}$, we have, for $\beta^{-1} = T = 0$,

$$n(x) = \pi^{-1}\cot^{-1}(\pi x/U_c) , \tag{20}$$

where $U_c = \pi V^2 \nu(0)$, and $x_c = \epsilon_F = 0$. U_c increases with temperature, and for $T \gg U_c(0)$, $U_c(T) \sim 4T$.

We may rewrite (15) as

$$F(H^{\text{eff}}) = \text{const} + \tfrac{1}{2} C\Big(\sum_\sigma \langle n_{d\sigma}\rangle\Big)^2 - U\langle n_{d\uparrow}\rangle\langle n_{d\downarrow}\rangle + \sum_\sigma \int_0^{E_\sigma^{\text{eff}}} n(x)\,dx . \tag{21}$$

The full variational function is the left-hand side of (6), and we will write it in terms of the E_σ^{eff} as the variational parameters. Remembering that $\langle n_{d\sigma}\rangle$ is an arbitrary variational parameter to be eliminated using (14), while the expectation value $\langle n_{d\sigma}\rangle_{H^{\text{eff}}}$ is given by (19), the function is $F^{\text{HF}}(E_\uparrow^{\text{eff}}, E_\downarrow^{\text{eff}})$ given by

$$F^{\text{HF}}(x,y) = F(x,y) + \tfrac{1}{2} C(\{2E_d + (U-2C)[n(x)+n(y)] - (x+y)\}/(U-2C))^2 , \tag{22}$$

$$F(x,y) = \text{const} + E_d[n(x)+n(y)] + Un(x)n(y) - \tfrac{1}{2} C[n(x)+n(y)]^2 - \int_0^x zn'(z)\,dz - \int_0^y zn'(z)\,dz . \tag{23}$$

$F(x,y)$ is a smooth function of (x,y) and bounded below; it thus has an absolute minimum at a solution of

$$\frac{\partial F}{\partial x} = n'(x)[E_d - Cn(x) + (U-C)n(y) - x] = 0 ,$$
$$\frac{\partial F}{\partial y} = 0 . \tag{24}$$

From (22) we see that at this minimum, $F(x,y)$ and $F^{\text{HF}}(x,y)$ have the same value. Hence

$$F^{\text{HF}}(x,y) \geq F(x,y) \geq F(H^{\text{eff}} + H^{\text{corr}}) . \tag{25}$$

This inequality, with expression (23), is basic to our work, and we will use $F(x,y)$ as the variational function for estimating the true free energy. From (24), the equations for stationary values of $F(x,y)$ are the Hartree-Fock equations

$$E_\uparrow^{\text{eff}} = x = E_d + (U-C)n(y) - Cn(x) ,$$
$$E_\downarrow^{\text{eff}} = y = E_d + (U-C)n(x) - Cn(y) . \tag{26}$$

These equations themselves could have been derived more directly, but the variational function $F(x,y)$ is essential when multiple solutions of (26) exist, in order to determine which solution is

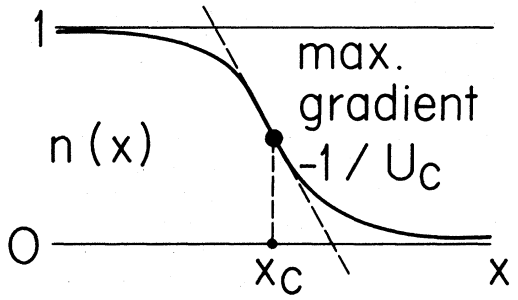

FIG. 1. Form of $n(x)$.

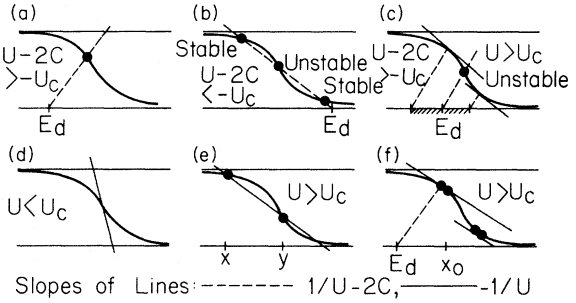

FIG. 2. (a) Unique nonmagnetic (NM) solution; (b) multiple NM solutions; (c) region of E_d with no stable NM solution; (d) no magnetic solutions for $U<U_c$; (e) magnetic solution; (f) critical magnetic solution.

globally stable.

We remark finally that when we find magnetic solutions with $x \neq y$, and $\langle \vec{S}_d \rangle \neq 0$, we have obtained those solutions with $\langle \vec{S}_d \rangle$ along with z axis. These solutions are rotationally degenerate with solutions where $\langle \vec{S}_d \rangle$ is in an arbitrary direction.

IV. CHARACTER AND STABILITY OF THE HF SOLUTIONS

We now study the HF equations (26): their properties are best illustrated graphically [Figs. 2(a)–2(f)]. We see that there is always a nonmagnetic solution, $E_\uparrow^{\text{eff}} = E_\downarrow^{\text{eff}} = x$:

$$x = E_d + (U - 2C)n(x) . \tag{27}$$

This is solved graphically in Fig. 2(a): for $U - 2C > -U_c$, there is a unique nonmagnetic solution; for $U - 2C < -U_c$, multiple solutions exist in a certain range of E_d. In particular, if such solutions exist, $1 + (2C - U)n' < 0$ for the middle one [Fig. 2(b)].

A locally stable solution is a minimum of F. To test for this we examine the second derivatives of F at solutions. It is convenient to take derivatives in the directions $u = (x+y)/\sqrt{2}$, $v = (x-y)/\sqrt{2}$. At a stationary point

$$\begin{aligned} F_{uu} &= -n'[1 + (2C - U)n'] , \quad F_{uv} = 0; \\ F_{vv} &= -n'(1 + Un') . \end{aligned} \tag{28}$$

For stability, both F_{uu} and F_{vv} must be positive. We defined U_c so that $0 > U_c n' \geq -1$; when $2C - U < U_c$ the nonmagnetic solution is both unique, and stable in the $x = y$ direction. If also $1 + Un' > 0$ the solution is locally stable. If $1 + Un' < 0$, the unique nonmagnetic solution is locally unstable against magnetism. This is only possible if $U > U_c$ [Fig. 2(c)]; we then see that there is a range of the parameter E_d where no locally stable nonmagnetic solutions exist. If $2C - U > U_c$, and $U < U_c$, solutions are stable against magnetism, but multiple nonmagnetic solutions may exist, and if they do, those with $1 + (2C - U)n' < 0$ are unstable. Unstable solutions lie between stable ones [Fig. 2(b)], and as E_d is moved through the range $(-\infty, \infty)$, a discontinuity will occur with a first-order transition between two locally stable nonmagnetic solutions.

In the remaining region of parameter space, $2C - U > U_c$ and $U > U_c$, nonmagnetic solutions may be unstable in either or both directions.

We now examine the magnetic solutions, $x \neq y$. Taking the difference between the two HF equations (26), and putting $(E_\uparrow^{\text{eff}}, E_\downarrow^{\text{eff}}) = (x, y)$, we have

$$x + Un(x) = y + Un(y) . \tag{29}$$

Figures 2(d) and 2(e) show that magnetic solutions only exist for $U > U_c$. For $2C - U < U_c$, $U > U_c$ the stable solution is magnetic for a range of E_d.

Examining the equations for $U = C$, we see that the two spin systems are decoupled at this value, and

$$F(x, y) = f(x) + f(y), \ (U = C) , \tag{30}$$

$$f(x) = E_d n(x) - \tfrac{1}{2} Un(x)^2 - \int^x z n'(z)\, dz . \tag{31}$$

The conditions $U = C$, $U > U_c$ imply that $2C - U > U_c$, so a region of multiple nonmagnetic solutions exists. Suppose $(x, y) = (a, a), (x, y) = (b, b)$ are two different locally stable nonmagnetic solutions, and E_d is precisely at the value where they are degenerate. Then the *magnetic* solution (a, b) is also locally stable, and has the same free energy. Evidently the line $U = C$, $U > U_c$ is the dividing line between discontinuous nonmagnetic behavior and magnetism. Examination of the free-energy surfaces about the solutions $(a, a), (b, b), (a, b)$ for $U \sim C$ shows that the global stability criterion for magnetism is indeed $U > C$, where the effective interaction between opposite spins is repulsive.

In the (U, C) half-plane, we can characterize the behavior of the minimum energy solution as E_d is varied from $-\infty$ to $+\infty$ (Fig. 3). In region I, the solutions are nonmagnetic, continuous. In

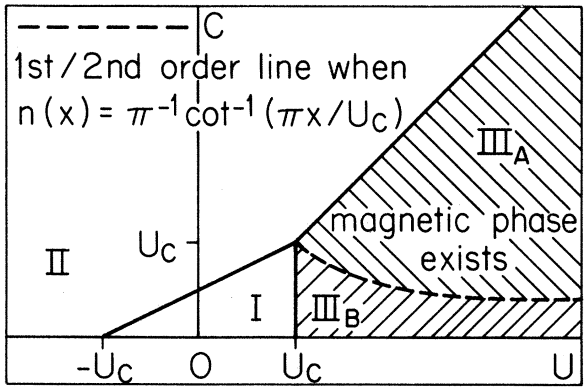

FIG. 3. Behavior of stable solution as a function of E_d. Always nonmagnetic: I—continuous, II—discontinuous. Magnetic phase intervenes: IIIA—first-order transition; IIIB—second order.

region II, they are nonmagnetic, with a first-order discontinuity at some intermediate value of E_d. In region III, a magnetic phase intervenes between two nonmagnetic phases.

The remaining question to settle is the nature of the two nonmagnetic-magnetic transitions that intervene in region III. Since a change in symmetry is involved, the transition may be either first or second order. A critical solution, where the magnetization goes continuously to zero always exists, and satisfies $1+Un'(x)=0$ [Fig. 2(f)]. However, as E_d is varied, a first-order transition may intervene before E_d reaches its critical value, rendering the second-order transition point inaccessible. A necessary, and—for our simplifying assumption that $n'(x)$ has only one minimum—sufficient condition for the transition to be second order is that the critical solution be locally stable. As the determinant of second derivatives vanishes at such a point, it is necessary to examine higher derivatives of F. The stability condition turns out to be

$$-\frac{n'''(x_0)}{n''(x_0)^2} < \tfrac{3}{2} U \frac{U-2C}{U-C}, \tag{32}$$

where $1+Un'(x_0)=0$. As n'' vanishes at x_c, the stability criterion for $U=U_c+\delta U$ is universal and is found to be $C<U_c-2\delta U$. Away from this region, the criterion depends on the specific function $n(x)$. For the canonical case $n(x)$ $=\pi^{-1}\cot^{-1}(\pi x/U_c)$, we find, for stability, $C<UU_c/(3U-2U_c)$. This is shown in Fig. 3. It is noteworthy that in the limit $C\to 0$, the magnetic transitions are always second order.

In Fig. 4, we show phase diagram in the (E_d, U) plane for three representative values of C. The vertical axis is chosen to be $E_d+\frac{1}{2}(U-2C)$, as this makes the horizontal axis the line of particle-hole symmetry (in the case of symmetric bands, at least).

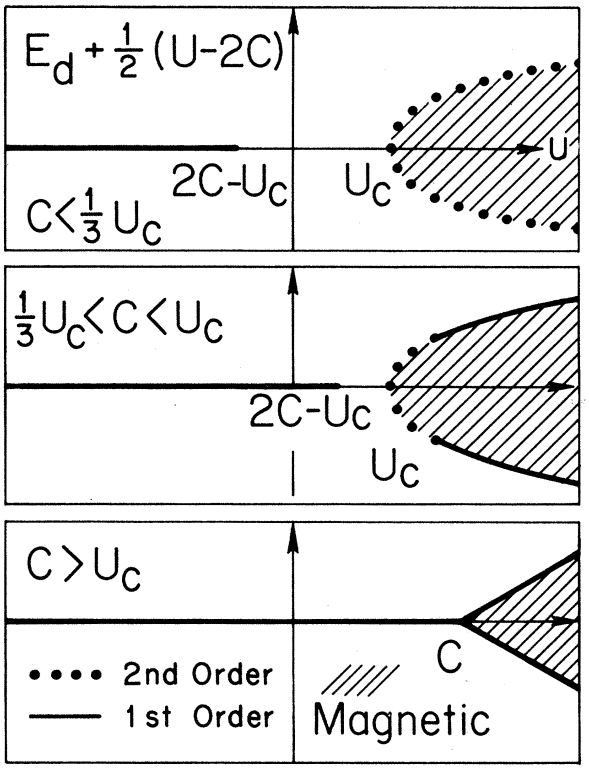

FIG. 4. Phase diagram in (E_d, U) plane, depicting the stable Hartree-Fock solution for three representative values of C, the effective attractive coupling between electrons due to the boson field. Lines of first- and second-order "phase transitions" and the region of "magnetic" solutions are shown. The first-order "phase transitions" mark models with a "mixed-valence" ground state; "magnetic" indicates the Kondo region.

V. COLLECTIVE-EXCITATION MODES IN THE RANDOM-PHASE APPROXIMATION

It is instructive to use the random-phase approximation (RPA) to examine the spectrum of collective excitations about HF solutions, and in particular to find the stability conditions which ensure that unstable modes with imaginary frequency do not exist.

The Hamiltonian, $H^{\rm eff}+H^{\rm corr}$, may be partially diagonalized about a general HF solution, and written

$$H^{\rm eff} = \text{const} + \sum_{j\sigma} \epsilon_{j\sigma} c^\dagger_{j\sigma} c_{j\sigma} + \sum_q \omega_q b^\dagger_q b_q . \tag{33}$$

$H^{\rm corr}$ is given by (10) and

$$c_{d\sigma} = \sum_j u_{j\sigma} c_{j\sigma} . \tag{34}$$

The RPA equations are obtained by linearizing the equations of motion of a particle-hole pair:

$$[H, c_i^\dagger c_j]^{\mathrm{RPA}} \simeq H^{\mathrm{RPA}}_{pq,ij} c_p^\dagger c_q . \tag{35}$$

The approximation is the replacement

$$c_i^\dagger c_p^\dagger c_q c_j \simeq \langle c_i^\dagger c_j\rangle c_p^\dagger c_q + \langle c_p^\dagger c_q\rangle c_i^\dagger c_j - \langle c_p^\dagger c_j\rangle c_i^\dagger c_q - \langle c_i^\dagger c_q\rangle c_p^\dagger c_j . \tag{36}$$

The RPA eigenvalue equations for the collective modes are easily solved, and we state the results.

First we define a generalized "susceptibility" for the local orbital:

$$\chi_{\sigma\sigma'}(\omega) = \sum_{ij} \frac{|u_{i\sigma}|^2 |u_{j\sigma'}|^2}{\omega - (\epsilon_{i\sigma} - \epsilon_{j\sigma'})} (\langle n_{i\sigma}\rangle - \langle n_{j\sigma'}\rangle) . \tag{37}$$

From (37) $\chi_{\sigma\sigma'}(\omega) = \chi_{\sigma'\sigma}(-\omega)$; with some manipulation using (18), it can be shown that

$$\chi_{\sigma\sigma'}(0) = -[n(E_\sigma^{\mathrm{eff}}) - n(E_{\sigma'}^{\mathrm{eff}})]/(E_\sigma^{\mathrm{eff}} - E_{\sigma'}^{\mathrm{eff}}) , \tag{38}$$

which reduces to $-n'(E_\sigma^{\mathrm{eff}})$ if $E_\sigma^{\mathrm{eff}} = E_{\sigma'}^{\mathrm{eff}}$.

On solving the RPA eigenvalue equations, four sets of collective modes are found. There is a conjugate pair of modes, related by time reversal, involving pairs like $c_{i\sigma}^\dagger c_{j-\sigma}$, with eigenvalue equation

$$1 - U\chi_{\sigma-\sigma}(\omega) = 0 . \tag{39}$$

The other two modes mix $c_{i\sigma}^\dagger c_{j\sigma}$ and $b^\dagger$, with eigenvalues given by

$$1 \pm [U - C(\omega)] \left(\frac{\chi_{\uparrow\uparrow}\chi_{\downarrow\downarrow}}{[1 - C(\omega)\chi_{\uparrow\uparrow}][1 - C(\omega)\chi_{\downarrow\downarrow}]} \right)^{1/2} = 0 , \tag{40}$$

$$C(\omega) = 2g^2 \sum_q \frac{|\alpha_q|^2 \omega_q}{\omega_q^2 - \omega^2} . \tag{41}$$

$C(\omega)$ is the ω-dependent electron-electron attraction mediated by the bosons. The coupling constant C is given by its static value $C(0)$.

In the nonmagnetic case, $\chi_{\sigma\sigma'} \equiv \chi$, there is a set of triplet spin-fluctuation modes in the x, y, and z directions with eigenvalue equation $1 - U\chi(\omega) = 0$ and (unnormalized) eigenmodes $U\vec{\sigma}_{\sigma\sigma'}\phi_{\sigma\sigma'}$ (summation over σ, σ' implied) where

$$\phi_{\sigma\sigma'} = \sum_{ij} \frac{u_i^* u_j}{\omega - (\epsilon_i - \epsilon_j)} (c_{i\sigma}^\dagger c_{j\sigma'} - \langle c_{i\sigma}^\dagger c_{j\sigma'}\rangle) . \tag{42}$$

There is also a set of singlet charge fluctuation modes $1 - [2C(\omega) - U]\chi(\omega) = 0$, with eigenmodes

$$[2C(\omega) - U] \sum_\sigma \phi_{\sigma\sigma} - 2g \sum_q \frac{1}{\omega - \omega_q} \alpha_q b_q + \frac{1}{\omega + \omega_q} \alpha_q^* b_q^\dagger . \tag{43}$$

Since $\chi(\omega) = \chi(-\omega)$, $\chi(i\alpha) > \chi(0) > 0$, and $0 < C(i\alpha) < C$, the stability conditions (no imaginary eigenvalues) are $1 + Un'(E^{\mathrm{eff}}) > 0$ (spin) and $1 + (2C - U)n'(E^{\mathrm{eff}}) > 0$ (charge). These are just the criteria we derived from our variational treatment of the free energy.

In the magnetic case, the spin modes split into a singlet parallel and a doublet perpendicular to $\langle \vec{S}_d \rangle$. Owing to the rotational degeneracy of the broken-symmetry magnetic solutions, there are zero-energy "Goldstone boson" modes corresponding to infinitesimal rotations of $\langle \vec{S}_d \rangle$; these arise from the perpendicular $\omega = 0$ doublet: for zero-energy modes, $1 - U\chi_{\sigma-\sigma}(0) = 0$; (38) then implies $E_\sigma^{\mathrm{eff}} + Un(E_\sigma^{\mathrm{eff}}) = E_{-\sigma}^{\mathrm{eff}} + Un(E_{-\sigma}^{\mathrm{eff}})$, which is precisely the condition (29) that magnetic solutions must satisfy. The other two modes mix charge and spin-modulus fluctuations. In the regime $U > C$, where a magnetic solution is globally stable, (40) indicates at least one of these two sets of modes is absolutely stable.

To summarize: These RPA results show that nonmagnetic minima of our free-energy functional $F(E_\uparrow^{\mathrm{eff}}, E_\downarrow^{\mathrm{eff}})$ correspond to HF solutions with stable RPA collective modes; magnetic "minima" are not truly stable, owing to the existence of zero-energy rotational modes.

VI. RELATION OF THE HF RESULTS TO THE TRUE PROPERTIES OF THE MODEL

The first thing to point out is that both the "phase transitions" in parameter space, and the existence of a "magnetic phase," are artifacts of the mean-field treatment; a zero-dimensional system, such as an impurity, coupled to a Fermi sea, which has infinitely many degrees of freedom associated with low-energy excitations, cannot exhibit phase transitions for finite values of the relevant coupling constant. The true ground state of our model is a singlet over the entire parameter space.[8] Nevertheless, the HF treatment reproduces all the gross features of the energetics, and our HF phase diagrams, when suitably reinterpreted, are a reliable guide to the exact properties of the model.

Two features of interest are seen in the phase diagram (Fig. 4). The first is the magnetic region; this is really a *Kondo* regime.[8] The residual interactions cause the magnetic spin vector $\langle \vec{S}_d \rangle$ to slowly precess, restoring rotational invariance, with a time scale given by the inverse of the Kondo temperature,[8] $T_K \sim (DU_c)^{1/2} \exp(-D/U_c)$, where $D^{-1} \sim (E_d + U)^{-1} - E_d^{-1}$. This behavior can only be obtained from sophisticated many-body renormalization treatments of the problem; the HF magnetic solutions are unsuitable as a starting point for such a scheme, as they introduce a

spurious infrared divergence. The up- and down-spin scattering phase shifts at the Fermi surface are different when the HF solutions are magnetic. By the Friedel sum rule,[9] this implies a nonzero net spin polarization of the Fermi gas around the impurity, in the $\langle \vec{S}_d \rangle$ direction. The "orthogonality catastrophe theorem"[10] implies that matrix elements between such states vanish identically if their spins are orientated in different directions; there is a strict *local* spin neutrality condition that HF states violate, and the correct ground-state properties cannot be recovered by taking simple combinations of such states.

The other interesting feature of the HF phase diagram is the existence of first-order "phase-transition" lines, where two locally stable solutions with different charge are degenerate. The low-energy behavior will be dominated by slow fluctuations between states like these, but again infrared difficulties prevent us from using the HF solutions as a starting point for investigating the true ground state. The line of first-order transitions between nonmagnetic solutions demonstrates this clearly: consider the canonical Anderson model with no boson coupling. As the band structure is symmetric about the Fermi level, a particle-hole transformation of one spin band shows that negative U models are equivalent to positive U models in a magnetic field $E_d + \frac{1}{2}U$. The negative U particle-hole symmetric case, on the first-order transition line, is isomorphous to the positive U zero-field symmetric case, which for large U exhibits the Kondo effect. Long time-scale *charge* fluctuations merely replace the *spin* fluctuations of the Kondo regime: the same time-scale T_K^{-1} is present. This behavior persists for a region of E_d of width $\sim T_K$, about the first-order transition line, corresponding to the persistence of the Kondo effect in weak magnetic fields. This correspondence can be continued into the $C \neq 0$ region and to models with nonsymmetric bands: all nonmagnetic charge fluctuation states are isomorphous to the Kondo problem.

The infrared problems with these HF states are related to the fact that the local charge (again given by the Friedel rule) is discontinuous across first-order HF phase boundaries, and again an "orthogonality theorem" shows that there are no matrix elements connecting states with different local charge, so taking a linear combination cannot improve the free-energy estimate.

Charge fluctuations also involve the relaxation of the boson field, with its own characteristic time scale, which we have left unspecified; if this is comparable to or smaller than T_K, it will play an important role too. If, as in the Tomonaga model, $f(\omega)$ is linear as $\omega \to 0$, an "orthogonality theorem" applies to it too. A particularly interesting case is the first-order transition between magnetic and nonmagnetic phases, which inseparably combines all three aspects of the infrared problem—spin, charge, and boson fluctuations—as it only occurs when the boson coupling is strong.

All these low-energy problems remain to be tackled by some suitable renormalization scheme, but we expect that their resolution will be similar to, if not isomorphous with, that of the usual Kondo effect,[8] including "universality," scaling behavior, and the like.

VII. PINNING OF COMPOSITE SYSTEMS IN CHARGE-FLUCTUATION STATES

The essential rotational degeneracy that is resolved by the Kondo effect is common to the continuous range of models whose parameters lie in the magnetic sector of the phase diagram. In contrast, in the context of impurity models, the degeneracy of models whose parameters place them squarely on first-order HF phase boundaries seems accidental, and the chances that any physical realization of the model would be in such a charge-fluctuation state would seem remote. However, we present an argument showing that when a composite system, regarded as being made up of a collection of "isolated" impurities, is considered, it has a finite chance of being exactly in a charge fluctuation state.

In Fig. 5, we plot $N(E_d - \mu)$, the total charge on the impurity orbital, as a function of the bare parameter $(E_d - \mu)$, in the neighborhood of a "first-order transition."

Suppose the atomic concentration of impurities in the material is c, and there are n_0 electrons per atom to distribute. If the normalized density of states per atom is $\rho(\omega)$, the chemical potential

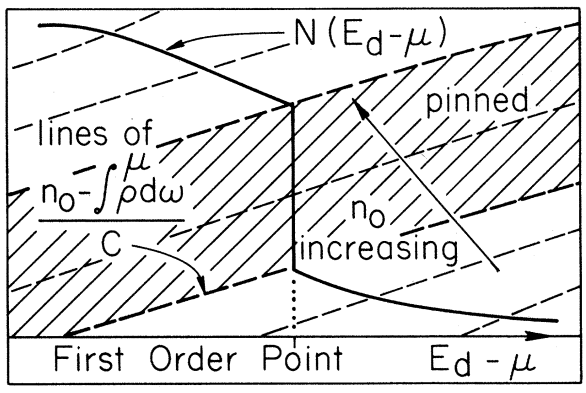

FIG. 5. Pinning of system in charge-fluctuation regime for a range of values of n_0.

is fixed by

$$\int_{-\infty}^{\mu} d\omega\, \rho(\omega) + cN(E_d - \mu) = n_0 . \tag{44}$$

This equation is solved graphically in Fig. 5 for a series of values of n_0. Because of the first-order discontinuity in $N(E_d - \mu)$, we see there is a certain range of n_0 for which $(E_d - \mu)$ is pinned precisely at the first-order point. [The exact curve for $N(E_d - \mu)$ will of course be rapidly varying but continuous near the "transition point," but the basic result still holds.]

VIII. DISCUSSION AND APPLICATIONS OF THE MODEL

To summarize, the gross properties of the Anderson model with coupling to a boson field are depicted by the Hartree-Fock phase diagrams in Fig. 4; C is the measure of the boson coupling. In the HF approximation, the bosons introduced lines of first-order transitions, which were absent in the physical case $U>0$ if $C=0$; these were identified as marking regions of mixed-valence behavior. We showed how composite systems may be pinned in such fluctuating states, and indicated that Kondo-like infrared problems were associated with a more exact treatment of the charge fluctuations.

The mixed-valence states fall into two categories; fluctuations between two nonmagnetic states, and fluctuation between a magnetic and a nonmagnetic state.

The first type, with fluctuations between ~0 and ~2 localized electrons, seem related to the resonant two-electron centers that pin the Fermi level, as proposed in Anderson's model of amorphous semiconductors,[6] and correspond to a fluctuating covalent bond. Here the bosons are lattice displacements.

The second type, where a magnetic state is involved, strongly resemble the experimentally observed "mixed-valence" states of certain rare-earth compounds.[4] Indeed we initially derived our model with these in mind, from a single-site version of the Falicov-Kimball model[3] combined with the Anderson model, representing an isolated rare-earth impurity in a d-band material. Of course the impurity f orbital is degenerate, but the fact that our nondegenerate model exhibits mixed-valence effects shows that this plays no fundamental role.

The key idea of our treatment in Ref. 5 is that the impurity orbital and the Wannier functions of the band have different point symmetries (d and f symmetry, respectively); when an interaction term between the charge in the impurity site Wannier functions and the impurity orbital is included, *two* sets of scattering channels, the slow f channels and the fast d channels are coupled. The d channels may then respond to screen the f channels so over-all charge neutrality is maintained during slow valence fluctuations. As the d band is very degenerate, the effective coupling necessary for neutrality is small, and the Tomonaga approximation,[2] where charge fluctuations in the d channels are replaced by a boson field, is valid. The boson bandwidth is much larger than the resonance width of the f channel, so the mean-field decoupling of bosons and fermions is a good approximation.

We showed that the mixed-valence charge fluctuations in the $C=0$ negative U model are isomorphous to the spin fluctuations of the $S=\frac{1}{2}$ Kondo model; by continuation, we argued this was generally true for all nonmagnetic charge fluctuation states. The magnetic mixed-valence states combine both aspects, spin and charge fluctuations. In future work, we aim to study the scaling behavior of this regime of the model, and to identify the appropriate "fixed point" of the renormalization procedure by similar techniques as those used on the Kondo problem.[8] Scaling behavior and "universality" is suggested by measurements of the low-temperature susceptibility of various mixed-valence metals, which show similar features on very different energy scales.[11]

Note added in proof. P. S. Riseborough, in *Proceedings of the International Conference on Valence Instabilities and Related Narrow-Band Phenomena, Rochester, N. Y., 1976,* edited by R. D. Parks (Plenum, New York, 1977), has studied the mean-field theory of this model using the Hubbard-Strattonovich functional-integral technique of Hamann, and has independently obtained some of the results presented here.

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APPENDIX

We derive the free energy $F(E, V)$ of the single-particle Hamiltonian

$$H(E, V) = \sum_k \epsilon_k n_k + E a^\dagger a + V(\psi^\dagger a + \text{H.c.}), \tag{A1}$$

where

$$\psi = \sum_k u_k c_k , \tag{A2}$$

and the $c_k^\dagger, a^\dagger$ are an orthogonal set of fermion creation operators.

We will use the Hellmann-Feynman theorem

$$F(\beta, H^0+H^1) = F(\beta, H^0) + \int_0^1 d\lambda \langle H^1 \rangle_{\beta, H^0+\lambda H^1} \tag{A3}$$

to write

$$F(E,V) = F(E',0) + \int_{E'}^{E} d\epsilon \langle a^\dagger a \rangle_{H(\epsilon,0)} + \int_0^V dv (\langle \psi^\dagger a \rangle_{H(E,v)} + \text{H.c.}) \ . \tag{A4}$$

The thermal averages are given by the Zubarev[12] thermal Green's functions $\langle\langle B; A \rangle\rangle_\omega$

$$\langle AB \rangle_{\beta H} = \frac{1}{2\pi i} \oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1} 2\pi \langle\langle B; A \rangle\rangle_{\omega, \beta H} \ , \tag{A5}$$

where Γ is the contour $(-\infty - i\epsilon) \to (+\infty - i\epsilon) \to (+\infty + i\epsilon) \to (-\infty + i\epsilon) \to (-\infty - i\epsilon)$.

The equations of motion for the Green's functions are easily solved in closed form:

$$2\pi \langle\langle a; a^\dagger \rangle\rangle_{\omega, H(\epsilon,0)} = 1/(\omega - \epsilon) \ , \tag{A6}$$

$$2\pi \langle\langle a; \psi^\dagger \rangle\rangle_{\omega, H(\epsilon,v)} = vf(\omega)/[\omega - \epsilon - v^2 g(\omega)] \ , \tag{A7}$$

where

$$g(\omega) = \sum_k \frac{|u_k|^2}{\omega - \epsilon_k} \ . \tag{A8}$$

Doing the integrals in (A4), for arbitrary E',

$$F(E,V) = F(E',0) + \frac{1}{2\pi i} \oint_\Gamma \frac{d\omega}{e^{\beta\omega}+1} \ln\left(\frac{\omega - E - V^2 g(\omega)}{\omega - E'}\right) . \tag{A9}$$

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*On leave of absence from the Cavendish Laboratory, Cambridge, England.

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